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Performance enhancement of white LED with TAG-Al_2O_3:Ce eutectic phosphor by partial Gd ion substitution

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ABSTRACT

In the traditional white LED, the phosphor is combined with the blue LED chip after mixed with the resin composite material. This combination affects the final light efficiency and color temperature, and cannot provide long-term stable work because of high emission and high temperature. Based on $Tb_3Al_5O_{12}$-Al_2O_3:Ce (TAG-Al_2O_3:Ce) eutectic, we developed the eutectic $Tb_{1.5}Gd_{1.5}Al_5O_{12}$-$Al_2O_3$:Ce ((TG) AG-$Al_2O_3$:Ce) to overcome the shortcomings of traditional phosphors. The eutectic was grown by an optical floating zone method. X-ray diffraction shows that the structure of (TG) AG-Al_2O_3 do not have significant changes compared to TAG-Al_2O_3, and the doped Ce^{3+} ions do not influence the basic structure of eutectic. Scanning electron microscopy shows that these materials have typical eutectic structure of sapphire and garnet phases, which can increase the length of the optical path to reduce the reflection loss and cause a higher luminous efficiency compared to the resin phosphor. Photoluminescence emission and excitation properties of (TG) AG-Al_2O_3 eutectic were investigated. The main excitation is in the luminous range (450 nm to 480 nm) of the blue LED chip for white LED. Compared with TAG-Al_2O_3:Ce, the emission peak is slightly shifted to the red, which cause the color temperature of (TG) AG-Al_2O_3:Ce eutectic LED is closer to natural light. The luminous efficiency of (TG) AG-Al_2O_3:Ce eutectic white LED is much higher than that of TAG-Al_2O_3:Ce eutectic. These results show that (TG) AG-Al_2O_3:Ce eutectic is promising phosphor for white LEDs.

1. Introduction

LED is the twentieth century emerging industry. Compared with traditional light like incandescent and fluorescent lamps, LED light source has more advantages such as long life, short response time, and it is usually made of environmentally friendly materials. Part of the fluorescent material in the blue LED irradiation can emit the yellow light. Blue and yellow light combine to form white light, the ratio of two kinds of light will affect the color temperature, color coordinates and other key performance parameters. The combination of blue LED and fluorescent powder is the main form of white LED, the fluorescent material properties directly affect the lumen efficiency, color coordinates, color temperature, brightness and other performance of white LED [1,2]. For the phosphor material, Yttrium aluminum garnet powder $Y_3Al_5O_{12}$:Ce (YAG:Ce)

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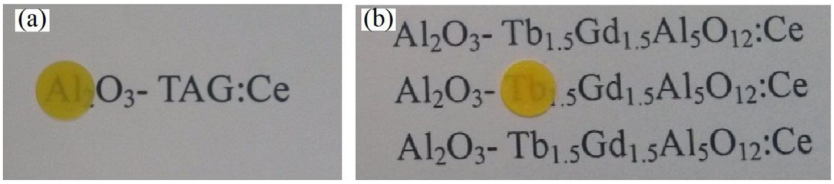

Fig. 1. (a)TAG-Al_2O_3 eutectic slice sample with the Ce^{3+} concentration of 1% (b) (TG) AG-Al_2O_3 eutectic slice sample with the Ce^{3+} concentration of 1%.

is currently widely studied and applied [3]. Replacing Y^{3+} ion by Tb^{3+} ion, fluorescent powder $Tb_3Al_5O_{12}$:Ce (TAG:Ce) have significant improvement in color rendering and color temperature because of the higher proportion of yellow light [4].

Fluorescent powder mixed silicone or epoxy resin have the advantages of simple process and low cost, but its drawback is poor heat dissipation, service life, light reflection loss and so on. So the researchers hope that the use of crystal materials instead of fluorescent powder to improve this problem. In 2013 Latynina et al reported that Gd-doped YAG:Ce single crystal encapsulated white LEDs were driven at a current of 40 mA with a high luminous efficiency, but the color rendering index was not good [5]. In addition, Lu et al. [6] and Gong et al. [7] also used the single crystal phosphor and achieved excellent results. Based on single crystal phosphor some scholars have proposed the YAG-Al_2O_3 eutectic structure. In this structure, YAG and Al_2O_3 crystals are coupled in three dimensions and form an interpenetrating network structure which is continuous at the atomic scale [8–10]. Because the refractive indices of YAG and Al_2O_3 are 1.78 and 1.83 respectively, the two phases with similar refractive index can increase the optical path length, and have higher light efficiency. Compared with single crystal, the low melting point of the eutectic crystal makes the crystal growth requirements, the cost and growth cycle are reduced. The YAG-Al_2O_3 eutectic phosphor can resist high temperatures up to 1700 °C, which may extend life of the white LEDs [11]. Sai et al. [12] studied the $Y_3Al_5O_{12}$- Al_2O_3 eutectic phosphor, and He et al. [13] studied the $Tb_3Al_5O_{12}$-Al_2O_3:Ce(TAG-Al_2O_3:Ce) eutectic phosphors, all of that achieved good results.

Based on the TAG-Al_2O_3: Ce eutectic phosphor, Ce^{3+} doped $Tb_{1.5}Gd_{1.5}Al_5O_{12}$-$Al_2O_3$ ((TG) AG-Al_2O_3) eutectic phosphor was grown by using Gd^{3+} ions to partially replace the Tb^{3+} ions in the eutectic base material. Without changing the TAG-Al_2O_3 eutectic structure, the partial substitution of the Gd^{3+} ion can adjust the excitation efficiency and emission wavelength positions. In the measurement of the LED white light chip composed of the (TG) AG-Al_2O_3:Ce phosphor, it is found that the color coordinate is in the yellow and white junction area which is high luminous area. Compared with the TAG-Al_2O_3:Ce eutectic phosphor studied with same Ce^{3+} doping concentration, the fluorescence lumen efficiency is better, and the color temperature of emitted light is 3586 K, which is closer to natural white light.

2. Experimental

2.1. Eutectic growth

(TG) AG-Al_2O_3:Ce eutectic were growth by optical floating zone technique. The molar ratios of TAG and Al_2O_3 in the TAG-Al_2O_3 substrate were 18.5% and 81.5%. The concentration of Ce^{3+} doped in the sample was 1.0%, and Tb^{3+} was partially substituted with Gd^{3+}, and the ratio was 1: 1. Raw material powder were ground for 12 h with alcohol in alumina containers by a micromill (model MM2000, Retsch, Haan, Germany), and pressed into compact rods at 210 mpa after drying. The raw material rods were sintered at 1200 ° for 10 h to obtain cylindrical rods with the size of 7–8 mm in diameter and 70–90 mm in length. During growth in optical floating zone furnace, the speed of the raw material rod and the crystal seed is 10 rpm and the descending speed is 6.5 mm/h and 4.5 mm/h respectively. The eutectic samples were slowly cooled to room temperature after growth and cut into slices with a thickness of 0.3 mm. At the same time, as comparative samples the TAG-Al_2O_3 with 1.0% Ce^{3+} doped were grown according to the research of He et al. [13]. Compared with TAG-Al_2O_3:Ce eutectic slice in Fig. 1(a), the light transmission performance of (TG) AG-Al_2O_3:Ce eutectic slices in Fig. 1(b) is slightly weakened, and the yellow color is deeper.

2.2. Characterization

After the eutectic sample was sliced, the structure was characterized by X-ray diffraction (Ultima IV Diffractometer, Rigaku, Japan). Tube voltage and current are 40 kV and 100 mA, respectively. Scanning speed is 2°/min, and scan width is 0.02° within $2\Theta = 10°–90°$. Microstructure was characterized by scanning electron microscope (SEM) (EM-30 PLUS£¬Korea£¬COXEM), and measured the energy dispersive spectroscopy. Working voltage is 15 kV and magnification is 2000. Photoluminescence was measured by a fluorescence spectrometer (Fluorolog Tau-3, Horiba, USA) which equipped with an Xenon lamp (JASCO FP6500, Japan) as an excitation source. Excitation wavelength used for measuring photoluminescence emission was 465 nm, and excitation spectra were measured at emission maxima. The eutectic crystals were cut into 5mm × 0.3 mm slices and fixed onto identical blue LED chip, as shown in Fig. 2. Both (TG) AG-Al_2O_3: Ce and TAG-Al_2O_3: Ce were measured at same conditions for comparison. Operated at 350 mA and 3.2 V, the blue chip emitted light with a peak